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Experimental determination of thermodynamical quantities in oxide mixtures and glasses

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Abstract

An overview of the experimental methods for the determination of thermodynamic functions in oxides systems is presented with a focus on two techniques: the solution calorimetry, which is applied in our laboratory both at room and at high temperature on oxide glasses and the Knudsen Effusion Mass Spectrometry (KEMS) which is under development in our team for activity measurement at high temperature. Emphasis is put on the description of the experimental setups and the measurement procedures. In this regard some key literature references are given added to some references concerning the measurements carried out on simplified glass systems.

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Keywords : Thermo-chemistry; Oxides, Glasses; Solution calorimetry; Knudsen Effusion Mass Spectrometry

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1. Overview of experimental methods

An exhaustive review of experimental methods for the determination of thermodynamic functions can be found in Kubaschewski et al. (1993) and in Komarek (1992). The methods can be classified into two main types: the calorimetric methods and the heterogeneous equilibrium methods.

The calorimetric methods are based on the direct or indirect measurement of the heat quantity evolved or absorbed by a sample undergoing a temperature change, a structural transition or a chemical reaction. A classification of the various types of calorimeters has been proposed by Hemminger and Höhne (1984) relying on

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their measuring principle, their mode of operation and their construction principle. The most frequently used sensors are thermocouples and thermopiles for respectively temperature and heat flow measurements. The heterogeneous equilibrium methods include the Electro-Motive Force (EMF) and the vapor pressure measurement methods. A very recent and comprehensive overview of the EMF method is given by Ipser et al. (2012). Among the different vapor pressure techniques, the Knudsen Effusion Mass Spectrometry (KEMS), alternatively named High Temperature Mass Spectrometry (HTMS), is the most versatile and powerful one which can deal with complex vapors in large pressure (from 10^{-12} up to 10^{-4} atm) and temperature (up to 2500-3000K) intervals.

The measurement methods for the thermal and the formation (or mixing) functions of a given phase, which can be a crystal, a liquid or a vitreous phase, are summarized in Table 1. The enthalpy change $\Delta H_{T_1}^{T_2}$ between two temperatures T_1 and T_2 is measured by isothermal drop calorimetry. For glasses, the inverse drop calorimetry, in which a sample held in a high temperature furnace is dropped into a room temperature calorimeter, is most frequently used (Stebbins and Carmichael 1983). The transition enthalpy $\Delta_{trs}H$ can also be measured by the same technique if the drops are repeated from two temperatures slightly below ($T_{trs} - \varepsilon$) and slightly above ($T_{trs} + \varepsilon$) the transition temperature T_{trs} or by temperature scanning techniques such as adiabatic calorimetry or Differential Scanning Calorimetry (DSC). The heat capacity (C_P) can be indirectly determined as the derivative of the enthalpy curve versus temperature obtained by drop calorimetry experiments performed at different temperatures. However, this method is very time consuming. Moreover if the heat capacity undergoes large changes within a small temperature range, DSC and adiabatic calorimetric operating in scanning mode are more accurate at low scanning rates. The absolute entropy can be derived by temperature integration of the heat capacity over temperature ratio if the heat capacity is measured from a temperature of few degrees Kelvin up to the temperature of interest. For example, this approach has been successfully implemented by Gailhanou et al. (2012) on a series of clay minerals by using low temperature adiabatic calorimetry in conjunction with DSC above room temperature. Similarly, the heat capacities of three ternary sodium borosilicate glasses have been measured by adiabatic calorimetry between 13 and 300K by Yamashita et al. (2001). The variations with temperature of the enthalpy and of the Gibbs energy are of course easily derived from the complete C_p curve.

Table 1. Functions relative to a single phase

Thermal functions		Formation or mixing functions	
Quantity	Method	Quantity	Method
$\Delta H_{T_1}^{T_2}$ J.mol^{-1}	• Isothermal drop calorimetry • Inverse drop calorimetry for glasses	$\Delta_f H$ or $\Delta_{mix}H$ J.mol^{-1}	• Direct reaction calorimetry • Solution calorimetry • Temperature coefficient in heterogeneous equilibrium (2nd law) • 3rd law knowing the absolute entropy of all the products and reactants
$\Delta_{trs}H$ J.mol^{-1}	• Isothermal drop calorimetry • Adiabatic calorimetry • Differential Scanning Calorimetry (DSC)	$\Delta_f G$ or $\Delta_{mix}G$ J.mol^{-1}	• Equilibrium constant of heterogeneous equilibrium: $\Delta G = RT \ln K$
C_P J.mol^{-1}.K^{-1}	• Derivative of ΔH with respect to T • Adiabatic calorimetry • DSC	$\Delta_f S$ or $\Delta_{mix}S$ J.mol^{-1}.K^{-1}	• Equilibrium constant of heterogeneous equilibrium: $\Delta S = \frac{\Delta H - \Delta G}{T}$
$\Delta S_{T_1}^{T_2}$ J.mol^{-1}.K^{-1}	$\int_{T_1}^{T_2} \frac{C_P}{T} dT + \sum \frac{\Delta_{trs}H}{T_{trs}}$		